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DESIGN AND SYNTHESIS OF FUSIBLE GLASS SOLDER WITH PREVIOUSLY ASSIGNED PROPERTIES

D. A. Geodakyan,[1] B. V. Petrosyan,[1] and K. D. Geodakyan[1]

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Experimentally substantiated recommendations on selecting compositions and technologies for synthesis of glass solders with assigned properties within the soldering temperature limits of 390 – 450°C and CLTE of $(60 – 70) \times 10^{-7}$ K^{-1}, designed for hermetically sealing the ceramic packages of integrated microcircuits are reported.

In many areas of science and technology, glasses, sitals, ceramic, and different composite materials are used as construction materials in addition to metals and alloys. Glass-solder materials — transition glass, glass cements, sitals, and glass solder compositions — are used for airtight joining of various materials. These materials are also used for interlayer insulation of integrated circuits, hermetic sealing of ceramic packages of microcircuits, preparation of pressure-seal feedthroughs in vacuum devices, dielectric resistive and conductor pastes for different applications, dielectric protective and decorative coatings on metals, alloys, etc.

Transition glasses, glass cements, and sitals are close to connectable materials in properties and composition. Glass solder compositions in most cases consist of a noncrystallizable glass base and crystalline fillers. For this reason, their properties can be varied within wide limits as a function of the properties and concentrations of the constituent components. This makes it possible to standardize the approaches in designing and synthesizing glass-solder compositions with previously assigned properties.

Despite the many glass-solder materials [1], there are no recommendations on selecting the compositions and technologies for synthesizing glass solders for concrete applications. For this reason, both the constituent components and the technologies for synthesizing such materials must be developed anew each time. This is a complicated task that requires a great deal of time and labor by highly trained specialists.

[1] Materials Science Scientific-Research and Production Co., Yerevan, Armenia.

We report experimentally substantiated recommendations on selecting the constituent components and synthesis technologies, obtained as a result of an analysis of the literature and our own studies in this area to facilitate the design and synthesis of maximally fusible glass-solder compositions designed for sealing the ceramic (Al_2O_3) packages of integrated microcircuits.

Many, sometimes contradictory, requirements are imposed on glass solders. The basic ones are: high wettability of the materials soldered, thermal and chemical compatibility with them, the required soldering temperature, certain mechanical, thermal, chemical, electrical, manufacturing, and performance properties.

Fusible glass-solder compositions designed for sealing integrated microcircuits in particular must have:

maximum low fusibility necessary for avoiding thermal immersion of the structural elements of the microcircuits, which would decrease the reliability of their work;

high electric resistance and low dielectric constant, necessary for the reliable operation of microcircuits in minimal sizes;

absence of or in the extreme case, low background radioactive radiation in the α-range to eliminate radiation immersion of the structural elements of the microcircuits.

Many of these properties of glass-solder compositions are determined by the glass base, which also predetermines the selection of additives to a great degree. For this reason, selection of the glass base is of primary importance.

Glasses synthesized in lead-borate eutectic (85% PbO, 15% B_2O_3) with ZnO, Al_2O_3, SiO_2, GeO_2, SnO_2, RO, PbF_2,

TABLE 1

Fusible glass group*	Control with DTA results					Crystallization, %, at 450°C for 1 h	Dilatometric control**	
	Temperature, °C			Number of uncrystallized glasses			CLTE, 10^{-7} K^{-1}, in the 20 – 200°C temperature range	initial deformation temperature, °C
	transformation transitions		initial crystallization					
	beginning	end						
I	238 – 352	271 – 399	274 – 514	3 from 42		100	–	–
II	274 – 364	320 – 418	330 – 611	29 from 86		10 – 100	89 – 120	300 – 385
III	209 – 430	249 – 463	263 – 520	0 from 17		100	–	–
IV	277 – 333	305 – 410	310 – 620	4 from 23		0 – 100	82 – 11	290 – 357
V	278 – 338	297 – 380	373 – 550	32 from 66		0 – 100	101 – 133	288 – 348
VI	345 – 450	385 – 490	485 – 714	0 from 7		60 – 100	–	–

* I: vanadate (molar content, %): 50 – 78 V_2O_5; 0 – 34 P_2O_5; 0 – 31 ZnO; 0 – 25 B_2O_3, PbO, CdO; 0 – 22 TeO_2; 0 – 10 BaO; 0 – 3 Al_2O_3, La_2O_3; 0 – 5 GeO_2.
II: lead (molar content, %): 45 – 86 PbO; 5 – 17 B_2O_3; 0 – 19 ZnO; 0 – 13 ZnF_2; 0 – 10 CuO, In_2O_3; 0 – 5 Bi_2O_3, CdO, MnO_2, GeO_2; 0 – 4 SiO_2, Al_2O_3, La_2O_3, TiO_2; 0 – 1 MgO.
III: lead-phosphate (molar content, %): 50 – 75 PbO, 25 – 50 P_2O_5 and $Pb(PO_3)_2$ with additives (wt.%): 2 – 6 SiO_2 and Al_2O_3, 2 – 10 ZnO.
IV: lead-borate (mass content, %): 57 – 85 PbO; 11 – 19 B_2O_3; 0 – 15 PbF_2; 0 – 11 ZnF_2, ZnO; 0 – 5 SiO_2, Al_2O_3, CuO, BaO, MnO_2.
V: lead-borate eutectic (mass content, %): 85 PbO, 15 B_2O_3 with additives 1 – 3% SiO_2, Al_2O_3, ZnO, V_2O_5, MoO_3, WO_3, NiO, and substitution of 1 – 3% B_2O_3 for BaO or 1 – 3% PbO for V_2O_5 and P_2O_5.
VI: lead-phsophate, zinc-borate (mass content, %): 75 – 95 $Pb(PO_3)_2$, 5 – 25 $Zn(BO_2)_2$, 5 – 10 Y_2O_3.

** Reported only for glasses with less than 50% surface crystallization.

ZnF_2, and other additives best satisfy these requirements (USSR Inventor's Certificate No. 1137088; Japanese Patent No. 55.100239, US Patent No. 4405722, RA 327) [2].

This is primarily due to the ready fusibility and low crystallizability of lead-borate glasses. However, high-lead glasses are harmful to human health and the environment. For this reason, we additionally analyzed the existing literature on other groups of fusible glasses [3]. More than 300 new glass compositions of the systems PbO – B_2O_3 – P_2O_5 – V_2O_5 – ZnO – CdO – TeO_2 – GeO_2 – PbF_2 – ZnF_2 – Tl_2O_3 with Al_2O_3, SiO_2, In_2O_3, CuO, MgO, La_2O_3, BaO, MnO_2, SnO_2, MoO_3, WO_3, and other additives were synthesized and investigated. In addition, chalcogenide (As – S – Se – I) glasses and compositions made from them were also obtained and investigated (RA Patent No. 327) [2 – 4].

The compositions of the glasses from this series of experiments, characterized by maximum fusibility, minimum crystallizability, and comparatively low CLTE, are reported in Table 1. It was not possible to find a valid substitute for high-lead glasses. For this reason, we recommend using the lead-borate eutectic with a small amount of modifying additives as the glass base for fusible glass-solder compositions for sealing the ceramic packages of integrated microcircuits. The compositions and properties of the best glasses are reported in Table 2.

TABLE 2

Glass	Approximate content, wt.%		Other components, 0.8 – 5.6 wt.%	Temperature, °C			Crystallizability*	Spreadability, mm, at 400°C for 20 min	CLTE, 10^{-7} K^{-1}, in 20 – 200°C temperature range	Resistivity, $\Omega \cdot$ cm, at 150°C	Dielectric constant**	Dielectric loss tangent
	PbO	B_2O_3		initial transformation transitions	initial deformation	final transformation transitions						
1	81	12	SiO_2, ZnF_2, PbF_2	285	305	318	50 – 60	14.2	111	1.2	19	21
2	84	13	SiO_2, Al_2O_3, ZnO	294	320	330	1 – 3	14.2	108	1.8	18	25
3	85	13	Al_2O_3, CdO	302	331	341	10 – 15	13.6	107	8.6	19	22
4	83	13	SiO_2, Al_2O_3, ZnO	305	333	345	1 – 2	13.4	107	1.5	18	23
5	79	13	Al_2O_3, ZnO, GeO_2	319	350	368	5 – 10	13.0	102	2.0	18	22

* At 400°C for 20 min + at 450°C for 1 h.

** At a frequency of 10^6 Hz and temperature of 25°C.

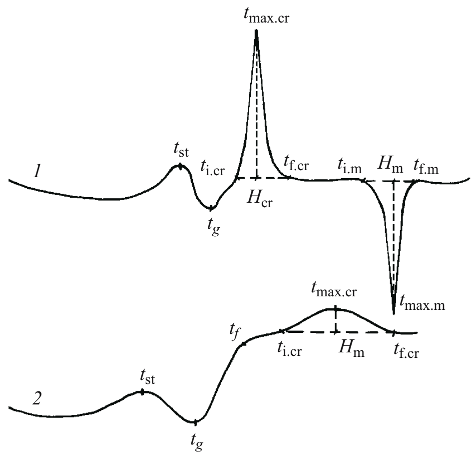

Fig. 1. DTA curves of glasses with bulk (*1*) and surface (*2*) crystallization.

Quality control for two basic criteria for the glass base, fusibility and crystallizability, by differential thermal analysis, which is characterized by simple instruments, simplicity, and rapidity of the experiment, high informativeness, accuracy, and reproducibility of the results, is recommended [5, 6].

The initial temperature of transformation transitions t_{st}, softening point t_g, completion of the transformation t_f, initial temperature, maximum rate, and completion of crystallization processes $t_{i.cr}$, $t_{max.cr}$, $t_{f.cr}$, melting point of crystals $t_{i.m}$, $t_{max.m}$, $t_{f.m}$, intensity of crystallization of the glasses H_{cr} and melting of crystalline formations H_m are determined with the DTA curves (Fig. 1).

Preference is given to glasses with minimum values of t_{st}, t_g, and t_f, minimum difference $t_f - t_g$, absence of or maximally high initial crystallization temperature. Glasses controlled with the DTA results are passed on for determining the spreadability and crystallizability at the required temperature for sealing microcircuits. The spreadability of the glasses can be determined on supports made of solderable materials, which also allows judging the wetting power of the glass. However, this requirement is not mandatory, since glass usually satisfactorily wets most construction materials.

The crystallizability (%) is determined by the degree of surface crystallization of samples that passed the spreadability test after additional holding for 60 min at a temperature 30°C higher than the temperature required for hermetic sealing. The surfaces of the samples are studied in reflected light under a microscope at magnification of 50 times.

Glasses with minimal crystallizability (maximum of 50%) and maximum spreadability (minimum of 13.5 mm at sealing temperature of 400 – 420°C, 8 mm sample diameter, 2 g weight) are selected for the subsequent studies. The CLTE and dilatometric temperatures of vitrification and initial deformation of the glasses are determined in the next stage. The lower these temperatures are and the closer the CLTE of the glass is to the CLTE of the soldered materials, the better it is. In the final stage, the dielectric properties of the glasses, which are necessary for selecting fillers together with the CLTE, are determined.

According to the recommendations, Glass 2 was selected as the base based on its properties (see Table 2).

Together with fusibility, glasses of the $PbO – B_2O_3$ system have high chemical activity, a tendency to reduce, and low stability with respect to water. These characteristics must be taken into account in melting, processing, grinding, and storing them. Special studies were conducted for this purpose. It was found that:

glass formation and fining of the glasses are complete at 700 – 800°C, but it is necessary to bring the melting temperature to 1150 – 1200°C or to stir the melt to increase the structural homogeneity; at melting temperatures below 1150°C or without stirring, the crystallizability of the glass increases; increasing the melting temperature above 1200°C is not useful due to the danger of evaporation of volatile components, B_2O_3 and fluorides, for example;

melting should be conducted in electric skull furnaces with indirect heating to prevent contamination of the glasses with refractory material and reduction of PbO;

glass granulate should be processed and specially ground dry to prevent formation of hydration shells on the surfaces

TABLE 3

Electric furnace	Crucible material	Crucible capacity, liters	Melting temperature, °C	Melting time, min	Stirring	Intensity of crystallization based on DTA data, mm	Degree of surface crystallization, %*
Muffle	Platinum	0.5	1150	90	None	0	2 – 3
High-frequency	″	12.0	1150	90	″	10	100
	″	12.0	1150	90	20 min	0	80
Skull:							
periodic, 5 kg/h	–	–	900	60	None	22	100
continuous, 3 kg/h	–	–	900	70	″	29	100
continuous, 5 kg/h	–	–	1200	60	″	0	3 – 10

* At 420°C for 10 min + at 450°C for 1 h.

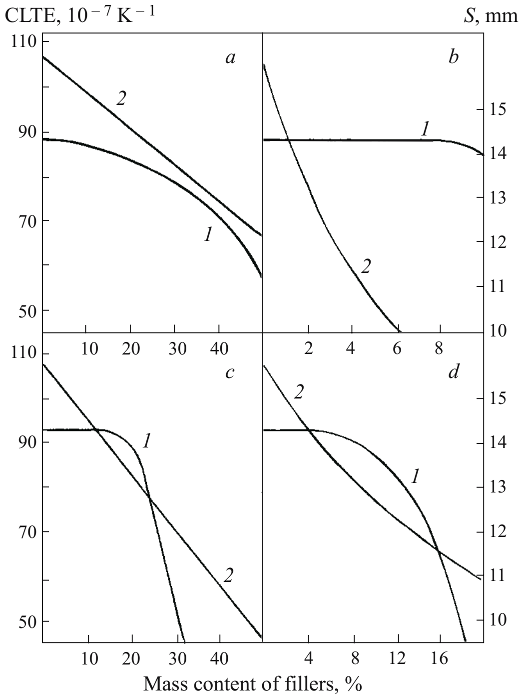

Fig. 2. Effect of filler content on spreadability S (*1*) at 420°C and the CLTE (*2*) of Glass 2 (see Table 2): *a*) lead titanate; *b*) β-eucryptite sital; *c*) zircon; *d*) cordierite sital.

of the glass particles as they significantly worsen the quality of partially fused compositions;

the specific surface area of glass powder after grinding must be within 1500 ± 100 cm^2/g and the maximum particle size should be 60 μm; complications related to obtaining highly homogeneous compositions, high dispersion, and reduction of PbO during grinding, arise at a lower dispersion;

use of accelerators (alcohols, for example) or compounds that reduce the degree of reduction of PbO by liberation of oxygen (PbO_2, Pb_3O_4, NH_4NO_3, etc.) is not recommended during grinding; the presence of these compounds in the glass sharply increases the porosity of the spread compositions;

the glass powder should be kept in a hermetically sealed container.

The effect of the conditions of melting Glass 2 (see Table 2) on the properties is shown in Table 3.

For thermal compatibility, for example, with aluminum oxide ceramic, the CLTE of the glasses in Table 2 must be reduced to the level of the CLTE of the ceramic, i.e., to $(66 \pm 2) \times 10^{-7}$ K^{-1}. Fillers with a perhaps low and even negative CLTE can be used for this purpose so that the spreadability of the glass solder will not especially decrease. Fillers that compensate for the thermal incompatibility of the components in the glass solder itself should be used parallelly. Other requirements for glass solders must also be considered: hermetic sealing of the joint, mechanical, chemical, electrical, dielectric, and other properties. For this reason, the fillers, their concentrations, particle size, and other indexes that affect the properties of the glass solder must be carefully selected.

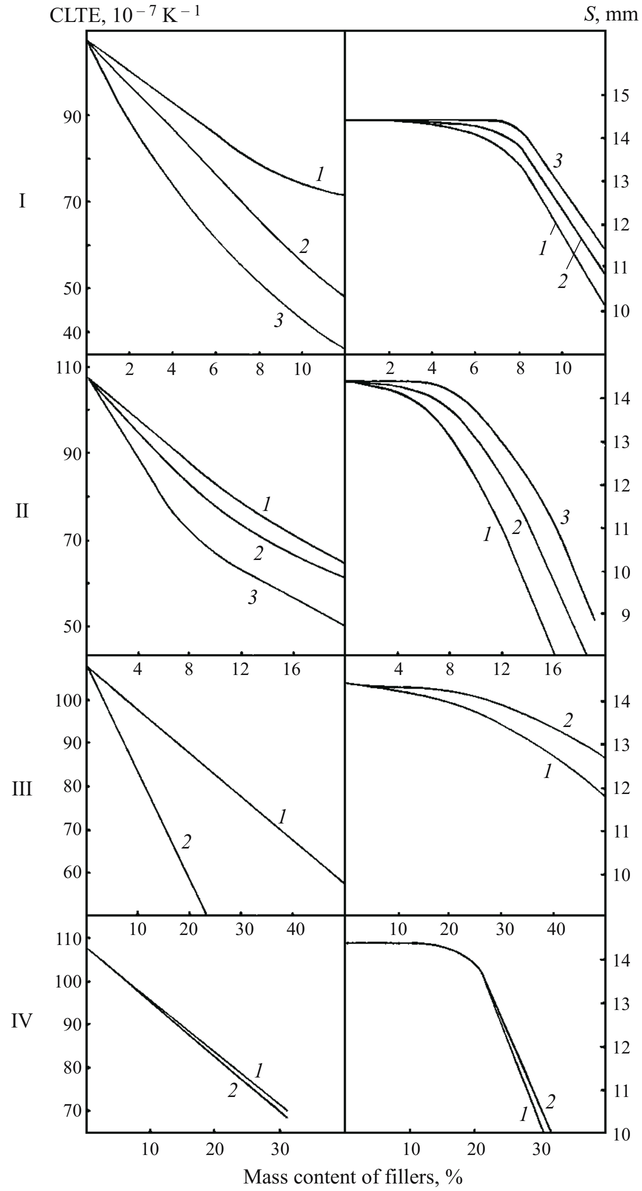

Fig. 3. Effect of the average filler particle size on CLTE and spreadability S at 420°C: I) β-eucryptite sital with particle size of 9.0 (*1*), 16.0 (*2*), and 22.0 μm (*3*); II) cordierite sital with particle size of 8.2 (*1*), 20.0 (*2*), and 33.5 μm (*3*); III) lead titanate with particle size of 24.2 (*1*) and 9.8 μm (*2*); IV) zircon with particle size of 4.6 (*1*) and 8.2 μm (*2*).

We investigated almost all of the appropriate materials (eucryptite, cordierite, calcium- and strontium-aluminoborate sitals, lead and aluminum titanates, wastes from airtight aluminum oxide ceramic) for this purpose. β-eucryptite and cordierite sitals, lead titanate, and zircon were the most promising (Figs. 2 and 3 and Table 4).

β-eucryptite sital ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) has a high negative CLTE (up to -150×10^{-7} K^{-1}) and correspondingly,

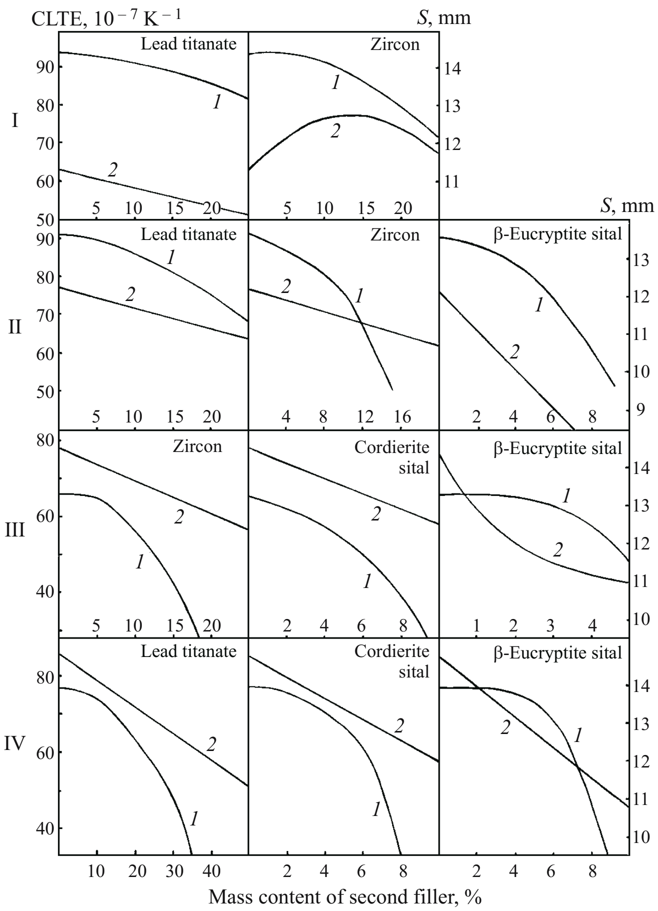

Fig. 4. Effect of a second filler on spreadability S (*1*) at 420°C and CLTE (*2*) of glass compositions: I) Glass 2 + 3% β-eucryptite sital; II) Glass 2 + 10% cordierite sital; III) Glass 2 + 30% lead titanate; IV) Glass 2 + 20% zircon.

the maximum specific decrease in the CLTE of the composition, which is a function of the average powder particle size.

TABLE 4

Filler	Average particle size, μm	Specific decrease: CLTE, 10^{-7} K^{-1}/%	Specific decrease: spreadability, mm/%	Quality of surfaces of samples hardened in air medium after determination of spreadability, background of microcracks
β-Eucryptite sital	9.0	3.68	0.84	Weak
	22.0	6.16	0.74	Thick
Lead titanate	25.0	0.61	0.25	Weak
	45.0	0.84	0.15	Medium
Cordierite sital	8.2	2.16	0.62	None
	33.5	2.23	0.23	Weak
Zircon	9.8	1.26	0.17	None
	24.3	1.27	0.17	″

Use of ETs 11-1 sital (TU 21-09.446.1-008–85) developed by SIG especially for fusible glass-solder compositions, is recommended. The CLTE of this material in the 20 – 300°C range is $(-125 \pm 5) \times 10^{-7}$ K^{-1}. Beginning at 350 – 400°C, the sital reacts intensively with the glass base, worsening the spreadability and microstructure of the composition, which requires special attention in selecting the granulometric composition of the powder. We recommend using sital powder with an average particle size of 25 ± 5 μm and the content of particles less than 15 μm in size should not be greater than 25% and the content of particles greater than 40 μm should not be any higher than 5% (PAShch.01100.00025 KTD).

Air separation and hydrolytic precipitation methods were investigated for fractionation of β-eucryptite sital by particle size. Three aqueous decantations of powder passed through a 100-μm mesh sieve is recommended as being comparatively simple. The large fraction (greater than 40 μm) is removed with the residue after 3-min precipitation of the aqueous suspension, and the dust-like fraction (less than 15 μm) is removed by pouring off after standing for 10 min. The average fraction obtained in this way can be dried to remove free (120 ± 10°C) and adsorbed (500 ± 10°C) moisture.

We also recommend keeping the β-eucryptite sital content in the compositions at less than 8 wt.% to prevent a significant decrease in the spreadability and worsening of the microstructure. It is useful to consider the changes in the partial decreases in these quantities in the presence of other fillers in calculations of the anticipated CLTE and spreadability values (Fig. 4).

Cordierite sital ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) has a moderately low CLTE [$(13 \pm 3) \times 10^{-7}$ K^{-1}] and dielectric constant (4 – 5) and for this reason is recommended for decreasing these indexes in glass compositions. In determining the granulometric composition, cordierite sital can be used without other fillers. The specific decrease in the CLTE of the

TABLE 5

Basic indexes*	Glass solder: SP66-2	Glass solder: S65-1	Glass solder: SKS-12
CLTE, 10^{-7} K^{-1}, in the 20 – 250°C range	66 ± 3	65 ± 3	66 ± 3
Sealing temperature, °C	395 ± 5	425 ± 5	445 ± 5
Dielectric constant**	25 ± 2	13 ± 2	11 ± 2
Dielectric loss tangent**	95 ± 5	88 ± 5	56 ± 5
Resistivity at 150°C	11.2 ± 0.2	11.4 ± 0.2	12.0 ± 0.2
α-radiation, particle/(h · cm^2)	0.12 ± 0.02	0.80 ± 0.10	0.40 ± 0.05

* The other parameters are within the limits of the requirements in the standards for packages and microcircuits.

** At frequency of 10^6 Hz and temperature of 25°C.

compositions with its content is relatively large, while the decrease in the spreadability is comparative small.

The dependence of these characteristics on the particle size is insignificant. For this reason, powder obtained after grinding cordierite sital (developed by SIG, TU 21-38-174–79) in ball mills to a specific surface area of 1300 – 1600 cm^2/g and passed through a 60-μm sieve should be used in glass-solder compositions.

Lead titanate, $PbTiO_3$, which has a CLTE of $(-10 \pm 5) \times 10^{-7}$ K^{-1}, is recommended for reducing the CLTE of the composition. Lead titanate has a comparatively low specific decrease in CLTE, but is stable with respect to glass bases and affects the spreadability comparatively little, which allows bringing its mass content in glass solders to 40%. The increase in the plasticity of the glass solder pastes, an increase in the thermal stability of the glass solders, and the comparatively insignificant dependence of the specific decreases in CLTE and spreadability on the granulometric composition of the powder are also advantages of lead titanate. Due to the last point, as in using cordierite sital, it can be managed without fine fractionation of the powder, and lead titanate passed through a No. 006 sieve and previously ground in a ball mill to a specific surface area of 1300 – 1600 cm^2/g can be used as an additive. The basic drawback of lead titanate is the high dielectric constant (more than 100 units), so that the presence of this filler is undesirable in glass solders with a dielectric constant of 10 – 15 units.

Zircon, $ZrSiO_4$, has a moderately low CLTE (approximately 40×10^{-7} K^{-1}) and plays the role of a buffer between the glass base and the β-eucryptite sital, increasing the thermal stability and degree of tightness of the joint. Without any other fillers, zircon significantly decreases the CLTE of the glass base and has almost no effect on the spreadability up to a 20 wt.% content. With other fillers (especially β-eucryptite sital), it increases the CLTE up to a 10 wt.% content and then slowly decreases it. The spreadability of the compositions decreases proportionally to the total concentration of fillers. Natural zircon — concentrated rock CZR, CZPE, CZZ — according to OST 48-82–81 can have a high radioactive background (10^{-9} Ci/g) so that it is not recommended for use in glass solders with stiff requirements for the presence of radioactive radiation in the α-range. In such cases, zircon obtained from the initial oxides with ceramic technologies should be used. The granulometric composition of zircon powder also does not especially affect the specific decrease in CLTE and the spreadability, so that powder obtained in the same way as cordierite sital or lead titanate can also be used in this case.

After preparation of the glass base and selection of fillers with the optimum particle size and concentrations, synthesis of the glass-solder composition consists of mixing the fillers with the glass base. Additional grinding of the components and contact of the composition with water should be avoided during mixing to attain the calculated parameters of the compositions. We tested almost all types of dry mixers (screw, drum, V-shaped, etc.). The V-shaped mixers were the best. They produced compositions with a high degree of phase homogeneity without additional grinding of the components. These mixers are extremely simple in design and servicing, are subject to modeling, and can provide sufficiently high reproducibility.

Based on model tests of V-shaped mixers, we recommend:

making the mixer of a solid conductive material to prevent contamination and electrification of the pastes which can cause aggregation of the powder and decreases the homogeneity of the compositions;

keeping the angle between the mixer arms within 35 – 45°, which corresponds to the most intensive mixing of the powders;

the degree of filling of the mixer should be no higher than the line of intersection of the arms;

calculating the optimum rotation rate with the centrifugal force equation:

$$\omega = \sqrt{\frac{8000}{R}},$$

where 8000 is the product of the square of the rotation rate of the model mixer by the radius of rotation of the point farthest from the axis of rotation; R is the radius of rotation of the most distant point of a real mixer;

determining the optimum mixing time with the equation;

$$\tau = 1200/\omega,$$

where 1200 is the product of the mixing time experimentally obtained in the model mixer (30 min) and its rotation rate (40 min^{-1}); ω is the frequency of rotation of a real mixer, min^{-1}.

Output quality control of fusible glass-solder compositions is recommended for the following parameters:

CLTE in the 20 – 200°C range according to OST 11.027.037–79;

sealing temperature according to a manufacturing test on parts of the packages of the corresponding integrated microcircuits according to OST 11.073.011–83; preliminary calculation of the sealing temperature is performed with the equation:

$$t_s = t_{s.ref} - 8(S - S_{ref}),$$

where t_s and $t_{s.ref}$ are the sealing temperatures of tested and reference samples of glass-solder compositions; S and S_{ref} are the corresponding spreadability values; 8 is an experimental factor obtained on samples 8 mm in diameter weighing 2 g; dielectric constant at 25 ± 10°C and frequency of 10^6 Hz according to OST 11.027.005–75; volume resistivity according to OST 11.027.006–83; other parameters at the client's request according to the active standards.

The final tests of the solder compositions should be performed on the corresponding articles according to the provisions in the standards.

Fusible glass-solder compositions for sealing the ceramic (Al_2O_3) packages of microcircuits whose properties are reported in Table 5 were designed, synthesized, tested, and proposed for mass production with the method described.

These compositions have a lower dielectric constant at the same sealing temperature or a lower sealing temperature with the same values of the dielectric constant than the existing glass solders.

In addition to glass solders designed for sealing aluminum-oxide packages for integrated microcircuits, lead-borate eutectic glasses with modifying additives and the crystalline fillers examined above can be used for synthesizing fusible glass solders for other applications, including compositions with CLTE of $(60 - 90) \times 10^{-7}\ K^{-1}$ and a soldering temperature of 350 – 500°C. The recommendations on melting and processing the glass base, preliminary processing of the components, and synthesis of the composition remain unchanged.

These recommendations will be useful both to consumers and to developers of fusible glass solders. The former can use them in establishing practically feasible technical requirements for glass solders and the latter can use them in designing and developing compositions that satisfy these requirements.

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